

DETERMINATION OF
ADHESION TENSION OF LIQUIDS
AGAINST SOLIDS

A MICROPHOTOGRAPHIC METHOD

A Dissertation

Submitted in partial fulfillment of the requirements for
the Degree of Doctor of Philosophy in the
University of Michigan

Ann. Arbor.

BY
ERNEST JOSEPH MERRILL

1929

DETERMINATION OF
ADHESION TENSION OF LIQUIDS
AGAINST SOLIDS
A MICROPHOTOGRAPHIC METHOD

A Dissertation

Submitted in partial fulfillment of the requirements for
the Degree of Doctor of Philosophy in the
University of Michigan

BY
ERNEST JOSEPH MERRILL

1929



The author desires to express his most sincere appreciation of the wholehearted interest, the helpful advice, and kindly direction of Professor F. E. Bartell, director of the work of this dissertation.

He also wishes to thank the American Petroleum Institute for their assistance in this investigation which has been carried on as a part of their Project No. 27.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41551510_0144

Contents

1.	Introduction	I
2.	Photomicrographic method	2
3.	Experimental method and apparatus	3
4.	Equilibrium contact angles	6
5.	Preferential adsorption	8
6.	Adhesion tension values from contact angles	9
7.	Conclusions	13

DETERMINATION OF ADHESION TENSION OF LIQUIDS AGAINST SOLIDS. A MICROSCOPIC METHOD FOR THE MEASUREMENT OF INTERFACIAL CONTACT ANGLES

The primary purpose of the present investigation was to obtain evidence concerning the validity of certain assumptions made in the development of the method of Bartell and Osterhof¹ for the determination of adhesion tension of solids against liquids. It was desired to obtain an independent check on the contact angle values and the corresponding adhesion tension values as determined by them. In their work contact angles were determined indirectly by a pressure of displacement method; in the work described herein, contact angles were measured directly by a microscopic method.

In this paper only a brief review of the pressure of displacement method can be included. Over a century ago Thomas Young² pointed out that a simple relationship existed between the different interfacial tension values of interfaces in contact and the resultant angle of contact formed by their intersection, and proposed that the following relation should hold,

$$S_1 - S_{12} = S_2 \cos \theta_{12} \quad (1)$$

S_1 = the surface tension of the solid.

S_2 = the surface tension of the organic liquid.

S_{13} = the interfacial tension of water against the solid.

S_{23} = the interfacial tension of water against organic liquid.

A_{12} = the adhesion tension of an organic liquid against a solid.

A_{13} = the adhesion tension of the water against the solid.

θ_{12} = the liquid-air-solid contact angle.

θ_{23} = the interfacial contact angle between liquid-liquid interface and the solid.

Freundlich³ more recently suggested that the adhesion tension of a liquid against a solid (A_{12}) should be given by the expression,

$$A_{12} = S_1 - S_{12} = S_2 \cos \theta_{12} \quad (2)$$

If the contact angle formed by a liquid-air-solid system were greater than a zero angle, then with equation (2) the adhesion tension value for the liquid against solid could be determined by measuring the surface tension of the

¹ Bartell and Osterhof: *Ind. Eng. Chem.*, **19**, 1277 (1927).

² *Phil. Mag.*, **1805**, 165.

³ "Colloid and Capillary Chemistry," 157 (1926).

liquid and the angle of contact. In a few instances this procedure is possible, but with nearly all liquids the contact angle is zero and hence the adhesion tension values become indeterminate. To overcome this difficulty, Bartell and Osterhof made use of the following formulation:

$$A_{13} - A_{12} = S_{12} - S_{13} = S_{23} \cos \theta_{23} \quad (3)$$

With the A_{12} value determined for a single liquid by equation (2), it was possible, by obtaining the interfacial tension of liquid against liquid, S_{23} , and the interfacial contact angle, θ_{23} , to determine the adhesion tension of water, A_{13} , according to equation (3). When once the adhesion tension of water was thus determined, the adhesion tension of other (organic) liquids against the solid could be found by using the same equation and again determining the interfacial tensions and the contact angles of these other water-organic liquid-solid systems.

In order to measure contact angles, Bartell and Osterhof used an apparatus consisting of a cell with an inlet tube at one end and an attached manometer at the other. In one half of the cell was packed water-wet solid while in the other half, the organic liquid-wet solid. When powdered silica was used as the solid material, the water tended to displace the organic liquid from the powder and in so doing set up a pressure which was read with a manometer. Assuming that the pores of the powder served as a multiple capillary system, and assuming that an equilibrium contact angle was formed in each of the pores, they calculated the value of this contact angle by the formulation,

$$\cos \theta_{23} = gPr/2 S_{23},$$

in which g = gravitational constant.

P = manometer pressure in gms/cm².

r = average effective radius of all capillaries.

In accepting measurements of this nature it is evident that three fundamental assumptions were made:

(1) That the fine pore structure of the solid is equivalent to a large cluster of single capillary tubes.

(2) That within each system a state of equilibrium is finally reached which includes in effect an equilibrium contact angle in each pore.

(3) That the formulations of Young and of Freundlich, and likewise their own derivations from these, are sound and hence give valid results.

It is the substantiation of all three of these hypotheses that this paper primarily undertakes.

The Photomicrographic Method

Casual microscopic observations of liquid-air-solid menisci and of liquid-liquid-solid interfaces set up in small capillary tubes suggested that true

representations of these might be secured by means of a photomicrographic apparatus. Then if it could be shown that such interfaces, when located in small capillaries, are either hemispherical or sectors of spheres, or that the variance therefrom is so small as to lie within the range of other experimental errors, it should be possible to project these photographic images upon the screen under large magnification and to make a fairly accurate measurement of the contact angles. Transparent capillary tubes were made available by using transparent quartz. This material was desirable since much of adhesion tension data obtained in this laboratory had been procured with silica.

Experimental Method and Apparatus

Satisfactory capillary tubes with diameters ranging from 0.2 mm. to 0.6 mm. were drawn from larger sized transparent quartz tubing. Only those were accepted for use which were found to have a uniform cylindrical bore. At first attempts were made to clean the tubes after drawing them. After much experimentation it was found that the washing of the inside walls of the tubes with acids produced undesirable changes on these surfaces and hence the practice thereafter was to use tubes just as taken from the fire in the drawing process. Glass capillaries were prepared for use in the same manner.

The method of studying the curvature and the contact angle was that of obtaining the photomicrograph of the liquid interface or meniscus upon a photographic plate which could be used as a lantern slide. With this negative, projections were then made upon a screen of white paper.

The photomicrographic apparatus consisted of an arc lamp, condensers, filters, heat absorption cell, adjustable light shutter, an immersion cell with constant temperature control for the capillary tubes, a microscope, an attached camera and a projection lantern.

Perhaps the greatest difficulty encountered in the work was that of overcoming the effect due to the different indices of refractions of the various parts of the different systems. This applied to the tube material, the liquid contained within, and the air or second liquid. It will be evident that the simplest system to study would be one composed of a liquid, air and a solid of which the liquid and the solid have the same index of refraction. An example of this kind is that of carbon tetrachloride-air-silica. By using an immersion liquid in the immersion cell which also had the same index of refraction as the silica, there would come through the microscope to the photographic plate a true image of the meniscus and of the contact angle.

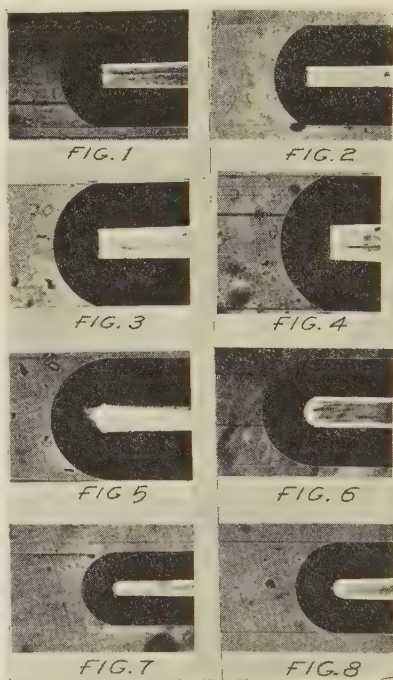
To determine whether the curvature of the menisci, in the size of capillaries that were to be used, were actually constant, a number of liquids possessing the same index of refraction as the material of the capillary walls were first studied. Figs. 1-8 inclusive show photographs of the menisci of

such liquids. It is apparent that the contact angles formed in the first four cases are greater than zero, and that those in the last four are zero or at least nearly so. Careful measurement showed them to be zero angles. By the aid of the projection lantern and a pair of dividers, a large number of such menisci were studied upon the screen at magnifications of 1000 diameters or greater. In no case could the slightest deviation from a constant curvature be found when the photographs had been accurately made with correct illumination. The need of the latter must be duly recognized. A small air bubble trapped within the liquid of one of the above systems serves as a desirable means of checking this factor. Illumination must be adjusted so as to give the circular outline of the bubble in the center of the tube image.

That the curvatures are constant is further substantiated by the fact that when angle values were later calculated upon the basis of this assumption, duplicate values for the same liquid in different tubes could be obtained even though the diameters of the tubes differed by as much as 300 percent. The work of Richards and Carver¹ also tends to check this conclusion.

Accepting the premise that the curvature of such menisci are constant, the method for measuring the value of the contact angle is shown in Fig. 9. ACB represents a cross section of the meniscus of the system, AB is the diameter of the tube and OB the radius of curvature. PQ is drawn tangent to the curve at point B. The angle of contact, θ , will then be equal to the angle θ' , and the measurement of the latter will give the value sought. When the contact angle is greater than zero the points A and B are readily located as shown. If the angle is of zero value, the radius of curvature and the radius of the tube will be identical.

Not all liquids have the same index of refraction as that of the material of the capillary wall. With such liquids the meniscus will appear distorted, Fig. 10, and a need of some modification of the previous method might at first thought appear to be demanded. The premise of the constant curvature of the meniscus will, however, still stand, for there is no reason for believing that the refractive index of a liquid will in any way affect the meniscus curvature. Furthermore, it is apparent that the point C on the meniscus, Fig. 11, will appear in its true position regardless of refractive index, since the light from this point will pass directly through the liquid and on through the wall



¹ Richards and Carver: *J. Am. Chem. Soc.*, **43**, 827 (1921).

of the tube without deflection. Observations will further show that, in spite of the differing indices of refraction of the liquid and the wall of the tube, the true positions of A and B are clearly indicated, due to the difference in light dispersion produced by the liquid and the air at the line of intersection. And

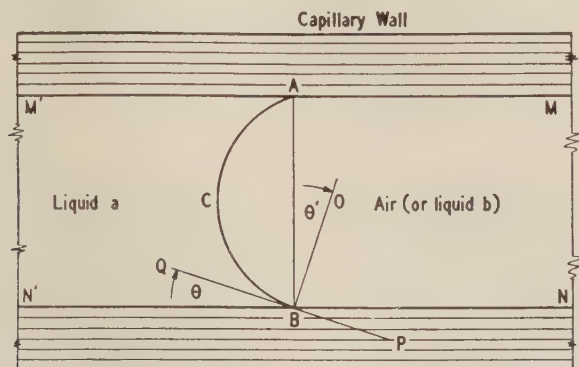


FIG. 9

Contact Angle. Liquid (or liquids) with index of refraction same as that of capillary wall.

so, while the meniscus will appear to be, in such cases as these, either in some position as $A'CB'$ or as $A''CB''$, the true positions of A, C, and B will still establish the true curvature and thus serve as the basis for measuring the true contact angle. The method is in effect the same as was used in the previous case.

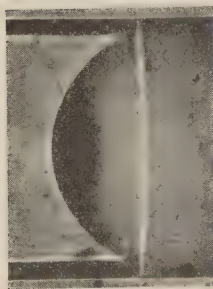


FIG. 10

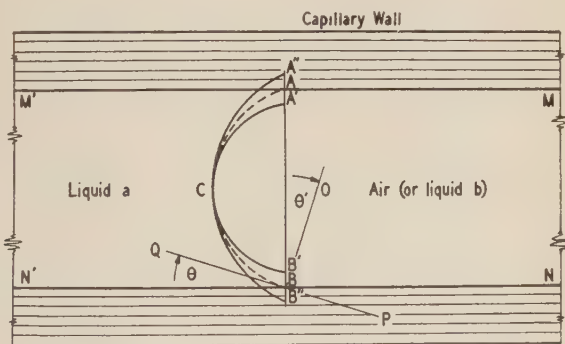


FIG. 11

Contact Angle. Liquid (or liquids) with index of refraction different from that of capillary wall.

Liquid-liquid-solid Systems.—In bringing the surfaces of two liquids together in a capillary tube for the measurement of the interfacial contact angle, a small amount of the organic liquid was first allowed to rise in the end of the tube. Water was then permitted to displace the organic liquid so that the water-organic liquid interface was carried to some convenient position in the capillary. The water end of the tube was then quickly sealed. The capillary was then kept at a constant temperature.

In a manner identical with that used to determine the type of curvature of the meniscus of the liquid-air-solid systems, liquid-liquid-solid interfaces were likewise found to possess constant curvatures. In determining this, pairs of immiscible liquids, each having the same index of refraction as the capillary wall material, were brought together and a study made as before. Figs. 12 and 13 show photomicrographs of two such interfaces. For liquids having different indices of refraction the discussion given above applies. The method used for measuring the interfacial contact angle was identical with that of the liquid-air-solid systems.

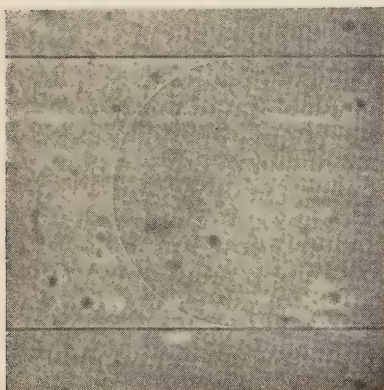


FIG. 12

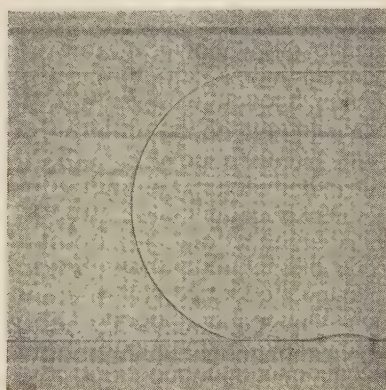


FIG. 13

The values of some liquid-air-solid and of liquid-liquid-solid contact angles as formed in capillaries of silica and of different glasses are given in Tables I and II.

Equilibrium Contact Angles

Much discussion is to be found in the literature relative to the formation of equilibrium contact angles between liquids and solids. Rayleigh¹ appears to have been one of the first to note the presence of the so-called advancing and receding contact angles. His work was confirmed by that of Miss Pockels.² Sulman³ concluded that "when a liquid reaches its final state of equilibrium by spreading over the dry surface of a solid, the contact angle is greater than when the liquid reaches its final state of equilibrium by receding from a previously wetted surface." He calls this the "hysteresis" of the contact angle, suggesting that the difference in the two angles is due to a changing surface tension of the solid once it is wet by the liquid. This view is shared by Bosanquet and Hartley.⁴ Adams and Jessup⁵ choose to consider this phenomenon as caused by friction of the liquid and the solid. Thus

¹ Rayleigh: *Phil. Mag.*, **30**, 397 (1890).

² Pockels: *Physik. Z.*, **15**, 39 (1914).

³ Sulman: *Trans. Inst. Min. Met.*, (1920).

⁴ Bosanquet and Hartley: *Phil. Mag.*, **42**, 456 (1921).

⁵ Adams and Jessup: *J. Chem. Soc.*, **127**, 1863 (1925).

additional energy is expended in order to overcome friction as the liquid moves out over the solid surface. Still others¹ conclude that the energy of adsorption of the liquid by the solid constitutes the determining factor.

TABLE I
Liquid-Air-Solid Contact Angles

Liquid	Silica	Pyrex	Lead Glass	Soda-lime Glass
Acetylene tetrabromide	28° 00'	30° 30'	22° 30'	21° 15'
Alphabromnaphthalene	21° 00'	20° 30'	6° 45'	5° 00'
Methylene iodide	33° 00'	29° 30'	30° 00'	29° 00'
Tribromhydrin	20° 15'	—	15° 30'	17° 00'
Alphachlornaphthalene	15° 00'	—	13° 30'	10° 30'
Iodobenzene	12° 10'	—	12° 15'	0° 15'
Bromoform	24° 30'	—	13° 00'	16°
Turpentine	0°	0°	0°	0°
Acetic acid	0°	0°	0°	0°
Glycerine	0°	0°	0°	0°
Carbon-tetrachloride	0°	0°	0°	0°
Xylene	0°	0°	0°	0°
Olive oil	20° 00'	21° 45'		
Oleic acid	27° 00'	27° 30'		

TABLE II
Liquid-Liquid-Solid Contact Angles
(Water—Organic Liquid-Solid)

Liquid	Silica	Lead glass	Soda-lime Glass
Acetylene tetrabromide	30° 30'	34° 15'	0°
Alphabromnaphthalene	33° 00'	37° 30'	0°
Methylene iodide	33° 30'	—	0°
Tribromhydrin	25° 15'	29° 30'	0°
Alphachlornaphthalene	25° 00'	30° 00'	0°
Iodobenzene	25° 30'	—	0°
Bromoform	24° 30'	22° 15'	0°
Benzene	28° 40'		
Toluene	35° 00'		
Carbon tetrachloride	25° 15'		
Hexane (synthetic)	25° 30'		
Nitrobenzene	42° 30'		
Carbon disulfide	42° 30'		
Amyl alcohol	55° 30'		
Butyl acetate	45° 00'		

¹ Ablett: Phil. Mag., 46, 244 (1923); Rideal: "Surface Chemistry" (1926).

A rigorous treatment of the subject of advancing, receding and equilibrium contact angles has been the subject of another investigation in this laboratory and so will not be further touched upon in this paper; suffice it to say that it now appears that where systems are contained in such small-sized capillary tubes as were used in this investigation, the forces of surface and interfacial tension appear to overcome any distorting effects due to gravity and should quickly bring a meniscus or interface to an equilibrium position and thereby establish an equilibrium contact angle. In this work it was not possible to bring two liquid surfaces together in a capillary tube at precisely such points as will later prove to be the true equilibrium contact points. Hence it is to be expected that some time must elapse before equilibrium will occur; usually from 10 to 24 hours is sufficient. Table III includes two series of readings

TABLE III
Advancing and Receding Contact Angles
Time required to reach equilibrium values
System 1. Water-benzene-silica

Time of standing	Value of angle	
	First tube	Second tube
1 hr.	15° 00'	30° 30'
6 hrs.	23° 15'	—
10 "	—	28° 50'
1 day	28° 45'	28° 20'
2 days	28° 00'	—
3 "	28° 30'	28° 40'
4 "	28° 40'	—

for contact angle values as they were measured over consecutive periods of time in two different water-benzene-silica systems. It will be observed that even though the first readings were greater or were less than those of the values finally obtained, both systems eventually gave angles of the same value. These readings are typical of those for all systems studied. Furthermore, the consistent duplication of contact angle values for the same liquids in different tubes which were set up at different times and therefore under somewhat different conditions, makes but one conclusion possible; namely, that although the angle formed before equilibrium conditions are reached may vary and may be either smaller or larger than the final angle, in due time a definite and constant angle will be formed. This latter angle we designate as the equilibrium contact angle. The evidence appears to be conclusive that with both liquid-air-solid and with liquid-liquid-solid systems in single capillary tubes a definite and reproducible contact angle is formed.

Preferential Adsorption

The equilibrium positions taken by the menisci of the liquid-air-solid systems were found to remain always the same no matter how long they were allowed to stand. On the other hand many of the liquid-liquid-solid

interfaces after weeks, or perhaps not until after months, of standing were observed to change and finally to form zero contact angles. A close study of these changing systems showed that water droplets were forming between the organic liquid surface and the wall of the capillary. These drops increased both in number and in size as time went on and then eventually all coalesced into one continuous film of water which completely surrounded the organic liquid column. Such a condition is nearly reached in the system as shown in the photograph of Fig. 14. It seems probable that as the two liquids stood in contact with each other they became mutually saturated. Since the silica has a greater attraction for water than for the organic liquid, the water was preferentially adsorbed by the silica, thus displacing the organic liquid. A slight change in temperature may have induced the initial drop formation and thereby caused the appearance of the water phase at the surface. Further adsorption and drop, or film formation, produces a growth of the film until it becomes continuous. When this happens the contact angle must necessarily become zero.



FIG. 14

The above behavior raises the question: have true equilibrium angles really been formed when admittedly the angle may eventually undergo change? Strictly speaking, the angle is not an equilibrium angle, otherwise it would not change. The change is probably due to an alteration in nature of the contiguous phases. The surface of the solid phase becomes altered, it passes from essentially a surface of pure solid to a surface of water, which phase finally covers the solid phase. The preferential adsorption of the water by the capillary wall material is a matter quite secondary to the original condition which gave the apparent equilibrium angle. This latter angle is probably in fact the characteristic angle for the phases in contact at the moment. Although considerable time may be required to obtain this angle, it will remain at a constant value for a comparatively long time. It is believed that this angle can be used to give fairly accurate values for adhesion tension. Further, it should be pointed out that interfacial contact angles measured by the microscopic method have shown good agreement with the interfacial angles obtained by the Bartell-Osterhof displacement pressure method.

Adhesion Tension Values from Contact Angles

It has been previously pointed out that a fundamental value in the determination of the adhesion tension of most organic liquids is the adhesion tension of water itself. To obtain this, it is necessary first to find some liquid or liquids which give a finite contact angle with air and the solid. Table IV gives such liquid-air-solid contact angle values, together with the adhesion tension values for the six liquids used. Table V gives the adhesion tension value of water for silica as determined independently using each of

these different liquids. The close agreement of the six values thus found for water is of much significance. Not only does it give a multiple check on the adhesion tension value for water against silica, but it goes far in checking the validity of the method used, together with all formulations which lie back of it. Similar data for these liquids and lead glass are also given in Tables VI and VII. Table VIII shows the contact angle and adhesion tension values for the organic liquids and soda-lime glass. The adhesion tension of water against this glass cannot be determined since all interfacial contact angles involved are of zero value.

TABLE IV
Liquid-Air-Silica Contact Angles, θ_{12}
Adhesion tension values, liquid-silica, A_{12}

Organic Liquid	θ_{12}	S_2^*	A_{12}
Acetylene tetrabromide	28° 00'	49.07	43.32
Tribromhydrin	20° 15'	44.76	42.00
α -Br-naphthalene	21° 00'	44.00	41.07
α -Cl-naphthalene	15° 00'	41.20	39.77
Iodobenzene	12° 10'	39.10	38.22
Bromoform	24° 30'	40.93	37.25

TABLE V
Interfacial Contact Angles, θ_{23}
Adhesion tension of water-silica, A_{13}

Organic Liquid	θ_{23}	A_{12}	S_{23}^*	A_{13}
Acetylene tetrabromide	30° 30'	43.32	38.32	76.34
Tribromhydrin	25° 15'	42.00	38.00	76.37
α -Br-naphthalene	33° 00'	41.07	41.57	75.93
α -Cl-naphthalene	25° 00'	39.77	40.24	76.24
Iodobenzene	25° 30'	38.22	41.34	75.53
Bromoform	19° 30'	37.25	40.35	75.28

Average value of $A_{13} = 75.92$

*All surface tension and interfacial tension values found in the data of this paper are those from the "Critical Tables" corrected to 25°C. In some instances temperature coefficient values were not available and values which appeared to represent justifiable approximations were used. Any errors thus introduced are surely not greater than the experimental errors of our method.

TABLE VI
Liquid-Air-Lead Glass Contact Angles, θ_{12}
Adhesion tension values, liquid-lead glass, A_{12}

Organic liquid	θ_{12}	S_2	A_{12}
Methylene iodide	30° 00'	50.16	43.73
Tribromhydrin	15° 30'	44.76	43.13
α -Br-naphthalene	6° 45'	44.00	43.61
α -Cl-naphthalene	13° 30'	41.20	40.05
Iodobenzene	12° 15'	39.10	38.70
Bromoform	13° 00'	40.93	39.86

TABLE VII
Interfacial Contact Angles, θ_{23}
Adhesion tension values of water-lead glass, A_{13}

Organic liquid	θ_{23}	A_{12}	S_{23}	A_{12}
Methylene iodide	Reaction, no results.			
Tribromhydrin	$29^{\circ} 30'$	43.87	38.00	76.18
α -Br-naphthalene	$37^{\circ} 30'$	44.16	41.57	76.59
α -Cl-naphthalene	$30^{\circ} 00'$	40.65	40.24	74.90
Iodobenzene	Reaction, no results.			
Bromoform	$22^{\circ} 15'$		40.35	77.30
Average value of A_{13} , (all independent) =				76.16

TABLE VIII
Liquid-Air-Soda Lime Glass Contact Angles, θ_{12}
Adhesion tension values, liquid-soda lime glass, A_{12}

Organic liquid	θ_{12}	S_2	A_{12}
Acetylene tetrabromide	$21^{\circ} 15'$	49.07	45.71
Tribromhydrin	$17^{\circ} 00'$	44.76	40.68
α -Br-naphthalene	$5^{\circ} 00'$	44.00	44.00
α -Cl-naphthalene	$10^{\circ} 15'$	41.20	40.20
Iodobenzene	0°	39.10	> 39.10
Bromoform	$16^{\circ} 30'$	40.93	39.24

By making use of the determined adhesion tension of water for silica and for lead glass, the adhesion tension of several other organic liquids for these solids were obtained and are given in Tables IX and X. The data of Table XI compares the values of the adhesion tension of several liquids as determined by this, the microscopic method, with those obtained by the Bartell-Osterhof displacement pressure (fine pore) method. It should be pointed out that the silica used in the latter method was specially treated tripoli or diatomaceous earth instead of transparent quartz. This would surely affect the results to a certain degree for the natures of the two surfaces would not be the same. A comparison should therefore be made on the basis of comparative values. For instance, the adhesion tension of water as determined by the two methods differs by nearly 7 dynes, a corresponding deviation holds also for the other liquid systems. Further evidence that the difference in values may be due to the different natures of the two forms of the silica is found in the work by Bartell and Miller¹. With the displacement pressure method the adhesion tension of water for fine sand was found by them to be 74.10 dynes, a value even lower than that found by this method for fused quartz. With the above in mind, it is quite apparent that the values for the different liquids agree very well, which fact gives substantial evidence as to the soundness of both methods, their fundamental formulations, and

¹ Bartell and Miller: unpublished.

developments, and at the same time indicates that the so-called adhesion tension of a liquid for a solid represents a specific and definite property of that system.

TABLE IX
Interfacial Contact Angles, Liquid-Water-Silica, θ_{23}
Adhesion tensions, organic liquid-silica, A_{12}

Liquid	A_{12}	θ_{23}	S_{23}	A_{12}
Water	75.92			
Amyl alcohol		55° 30'	4.96	73.13
Ethyl carbonate		55° 00'	12.65	68.74
Butyl acetate		45° 00'	13.17	66.60
Nitrobenzene		42° 30'	25.32	57.25
Toulene		35° 00'	35.86	46.54
Benzene		28° 40'	34.76	45.43
Carbon disulfide		42° 30'	48.10	40.46
Carbon tetrachloride		25° 15'	44.50	35.67
Hexane (synthetic)		25° 30'	51.00	29.90

TABLE X
Interfacial Contact Angles, Liquid-Liquid-Lead Glass
Adhesion tension, organic liquid-lead glass, A_{12}

Liquids	A_{13}	θ_{23}	S_{23}	A_{12}
Water	76.16			
Amyl alcohol		0°	4.96	<71.00
Ethyl carbonate		0°	12.67	<63.25
Butyl acetate		0°	13.17	<62.75
Nitrobenzene		27° 30'	25.32	53.50
Toluene		26° 30'	35.86	43.82
Benzene		0°	34.76	<41.66
Carbon disulfide		33° 40'	48.10	44.25
Hexane		36° 30'	51.00	34.92

TABLE XI
Comparison of Adhesion Tension Values; Fine Pore vs. Microscopic Methods

Liquids	A_{12} Fine pores	A_{12} Microscopic
Water	82.82	75.92
Butyl acetate	73.45	66.60
Carbon tetrachloride	40.69	35.67
Toluene	54.70	46.54
Benzene	52.43	45.43
Carbon disulfide	45.94	40.46

Conclusions

It is believed that this investigation has given the following rather conclusive evidences:—

1.—That equilibrium contact angles are formed when solid-liquid-air phases are in contact; likewise definite contact angles are formed between liquid-liquid-solid phases. These angles can be formed within capillary tubes; they are quite independent of the size of the tubes and can be measured fairly accurately.

2.—That the adhesion tension as measured is specific and definite for a given solid-liquid system.

3.—That the formulations used in the determination of adhesion tension were justified.

4.—That the data obtained by the microscopic method show good agreement with the results obtained by the Bartell-Osterhof pressure of displacement method and tends to substantiate the correctness of the assumptions made in connection with their work.

*Department of Chemistry,
University of Michigan.*

